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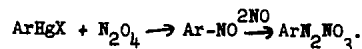
THE ACTION OF OXIDES OF NITROGEN AND NITRIC ACID ON MERCURY
 PARAFFINIC COMPOUNDS. UTILIZATION OF THE REACTION FOR THE
 INVESTIGATION OF THE NITRATION OF PARAFFINS

A. I. Titov and D. Ye. Rusanov.

Only one investigation, Bamberger's (1), deals with this reaction. Allow-
 ing N_2O_4 and N_2O_3 to act on dimethylmercury, he did not obtain the expected
 diazomethane, but isolated only a small amount of a crystalline product, to
 which he conjecturally assigned the structure of iminodiformo-hydroxamic acid.



The action of oxides of nitrogen and nitric acid on aryl mercury compounds has
 been well studied. According to the investigations of Bamberger (1) and
 Mesmeyanov (2), the reaction with oxides of nitrogen proceeds by the equation:



In our preliminary work with A. N. Baryshnikova (3) and M. G. Laptev (4),
 it was shown that nitric acid in the absence of oxides of nitrogen does not
 react at all with aryl mercury compounds or has only a destructive effect on
 them. In the presence of oxides of nitrogen, the reaction leads to the for-
 mation of nitroso compounds, diazonium salts, normal nitrophenols, mononitro
 derivatives, p-dinitro compounds, anomalous nitrophenols, and nitrosodiaryl-
 hydroxylamines in proportions depending on the conditions and structure of
 ArHgX . We established experimentally that the formation of all of these prod-
 ucts is dependent on the transformation of the nitro compounds that are formed
 first.

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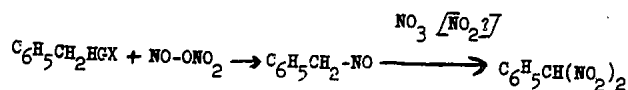
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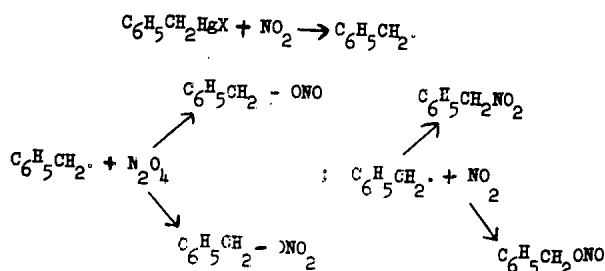
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As the original objects of investigating, the reaction of NO_2 with mercury paraffin compounds, we selected dibenzylmercury and benzylmercuric chloride, since we studied their expected conversions earlier. The fully substituted mercury derivative, as well as the mixed mercury derivative, reacted energetically with nitrogen dioxide, even at low temperatures. Under ordinary conditions, the reaction with nitric acid proceeded only in the presence of oxides of nitrogen.

Preliminary considerations led to two possible mechanisms for the reaction between nitrogen dioxide and benzylmercury. If we start from the assumption that the reaction will proceed in the same manner as for arylmercurial compounds through a preliminary formation of nitroso compounds, then, according to our previous investigations, the end product of the reaction must be phenyldinitromethane (5, 6):



On the other hand, if we assume that the fragment $-\text{HgX}$ plays the part of a mobile hydrogen in the paraffinic chain, then, according to our theory of nitration of saturated hydrocarbons by nitrogen dioxide in the absence of NO , phenyldinitromethane should, for all practical purposes, not form. The chief products of the reaction should be benzylnitrite, benzylnitrate, and phenylnitromethane (7, 8).



Experiment showed that the reaction with dibenzylmercury, as well as with benzylmercuric chloride, leads to the formation of benzyl nitrite, nitrate, and the products of their conversion under the stated conditions. A small amount of phenylnitromethane was also formed, but no phenyldinitromethane was detected.

Subsequent experiments also confirmed the applicability of our theory of nitration of saturated hydrocarbons to the reaction between nitrogen oxides or nitric acid and mercury paraffinic compounds. In accordance with the theory and results of investigation of the reaction with toluene, nitration of dibenzylmercury and benzylmercuric chloride in the presence of nitrogen oxides led to the formation of phenyldinitromethane or the product of its conversion, i.e., p-nitrobenzoic acid, depending on the conditions. Nitration at an elevated temperature under the conditions of almost complete dissociation of N_2O_4 resulted in phenylnitromethane as the principal product of the reaction.

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On the other hand, an essential difference between the nitration of toluene and of benzylmercury was cleared up in these same experiments. It developed that the reaction rate of mercury derivatives is incomparably greater than that of hydrocarbons, and that the interaction proceeds practically instantaneously. On the basis of a number of analogies, it can be assumed that the activation energy of the reaction of NO_2 with R_2Hg is by at least 30 kcal lower than that of the reaction with RH . For the mixed derivative R-Hg-Cl , the drop of energy will be, in accordance with the theory, less significant due to the electron-attracting action of the halogen.

The conclusions just stated were also justified for other mercury paraffinic compounds. Diethyl and di-n-butylmercury reacted with nitrogen dioxide very energetically, even at minus 10° , while the corresponding hydrocarbons react with nitrogen dioxide only at high temperatures. But, as distinguished from the reaction of NO_2 with benzylmercury, under these conditions the reaction proceeded only to the stage of formation of mixed mercury derivatives RHgNO_2 ; ethylmercury bromide and butyl mercury did not react at ordinary temperatures at all, while at 100° the reaction proceeded comparatively slowly. The lower reactivity of purely paraffinic derivatives in comparison to mercury compounds of benzene is found to be in complete agreement with our theory, since the activation energy for compounds of the first type must be 12-15 kcal higher than for the corresponding benzyl derivatives (5). This difference may not affect completely substituted mercury derivatives, but it does matter in the case of mixed ones. In accordance with theory, introduction of a nitro group strongly lowers the activity toward nitration; for example, 2,2'; 4,4' -tetranitrodibenzylmercury did not react at all with nitrogen dioxide under normal conditions. In accordance with our hypothesis (10) of the cryptoaromatic effect, cyclohexylmercuric bromide reacted with NO_2 at a normal temperature.

The high reactive capacity of mercury derivatives led us to the thought of using it in order to carry out nitration under such mild conditions as could not be achieved in a reaction with the hydrocarbons themselves. Due to this, it was possible to achieve a practical realization of other directions of the reaction or the preservation of its unstable products. Experiment justified our expectations. Thus, in the nitration of benzylmercuric chloride with nitric acid of 1.1 sp gr at a low temperature, diphenylfuroxan was obtained with a 40% theoretical yield. We foresaw in 1941 (9) the possibility of the formation of this product in nitration. We isolated it in a similar way upon formation by the action of an insufficient amount of nitrogen dioxide on dibenzylmercury - this corresponds to the conditions of its preparation from benzaldioxime and nitrogen dioxide (6) and hence to our theory.

We also used this method for the quantitative determination of yields of alkyl nitrites in the nitration of mercury paraffinic compounds and consequently, of the hydrocarbons themselves. In the nitration of di-n-butylmercury with nitrogen dioxide at minus 5° , the alkyl nitrite yield exceeded 15.5% of theory. Making this determination in connection with the nitration of n-butane itself is impossible. In the nitration of benzylmercuric chloride with nitric acid of 1.2 sp gr, a yield of benzyl nitrite amounting to 20% of the theoretical with reference to the initial product and of about 30% on the basis of the isolated product was obtained.

All that has been stated allows one to regard the investigation of the action of nitrogen oxides and nitric acid on suitable mercury paraffinic compounds as an excellent means of acquiring a more thorough knowledge of the nitration of the paraffin chain. It would seem that this method would in particular have a major role in the study of the nitration of the most inert hydrocarbons -- methane and its close homologs. An additional advantage of this method is the directed nature of the reactions. It is also possible to foresee another series of applications of this method as, for example,

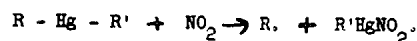
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determination of the relative ability of alkyls to change into the free radical state by means of investigating the reaction between nitrogen dioxide and unsymmetrical mercury paraffinic compounds.



We shall describe some of the experiments. Separation of the reaction products was done in the usual manner which we described earlier (6 - 8).

Determining the Yield of Nitrites and Nitrates.
Separation of Phenylnitromethane

1. 2 g of sodium nitrite were added during 30 min under stirring to a mixture of 100 ml of HNO_3 (sp gr 1.2) and a solution of 5 g of $C_6H_5CH_2HgCl$ in 40 ml of $CHCl_3$. This was followed by separation and washing of the organic layer with water and soda solution; from the soda extract 0.4 g of phenyldinitromethane were separated by acidification -- 15% of theory. After distilling off the chloroform, we added 20 ml of N/4 solution of sulfanilic acid and 5 ml of concentrated HCl to the residue which weighed 1.73 g, and stirred vigorously for half an hour at $3-5^\circ$. The mixture gave a sharp reaction for a diazo compound with betanaphthol; 12.1 ml of N/4 solution of nitrite were used in the back titration, which corresponds to a 13% theoretical yield of benzyl nitrite. After the titration, the mixture was extracted with ether. The solvent was then distilled and the residue treated with 1 ml of diethylamine to convert the benzyl nitrate into benzyldiethylamine, as described earlier (8); 0.17 g of the amine were obtained (7% of theory). In the experiment using 20 ml of nitric acid, the benzyl nitrite yield was 21% of theory based on the starting material and about 30% based on the isolated product.

2. To a solution of 2 g of N_2O_4 in 20 ml of $CHCl_3$ at minus 5° , 3.5 g of di-n-butyl mercury in 15 ml of $CHCl_3$ were added dropwise under stirring. After careful washing with water and a solution of soda, nitrite was determined as described above. The nitrite yield was 15% of theory.

Preparation of Phenylnitromethane

A solution of 10 g of benzylmercuric chloride in 50 ml of tetrachlorethane was added dropwise to a mixture of 25 ml of HNO_3 (sp gr 1.36) and 1 ml NO_2 heated on a water bath in a flask equipped with a reflux condenser. Two grams of a mixture of benzoic and p-nitrobenzoic acids, 1.4 g of phenylnitromethane boiling at 118° at 16 mm (33% of theory), and 0.6 g of residual oil were separated by a previously described method (7).

Preparation of Phenylfuroxan

Two grams of sodium nitrite were added over a period of half an hour to a mixture of 100 ml of HNO_3 (sp gr 1.1), 30 ml of $CHCl_3$, and 5 g of benzylmercuric chloride. After the usual treatment and distillation of the solvent, there remained 1.41 g of a crystalline mass, which, after washing with ether, yielded 0.72 g of colorless crystals. Purification by dissolving in chloroform and precipitation with alcohol gave a product melting at $115 - 116^\circ$. Its melting point was not lowered when it was mixed with phenylfuroxan synthesized according to Ponchio.

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